

# Catalytic Solubilization and Conversion of Lignocellulosic Feedstocks

## LANL Team

***T.A. Semelsberger (P.I.) , Kevin C. Ott (Co-PI),  
Rod L. Borup, & Roshan Shrestha***

***DOE Hydrogen Program Annual Merit Review,  
EERE: Hydrogen, Fuel Cells and Infrastructure Technologies Program  
Hydrogen Production and Delivery  
Washington, DC  
May 18-22, 2009***

pdp\_12\_semelsberger



**U.S. Department of Energy**  
**Energy Efficiency  
and Renewable Energy**  
Bringing you a prosperous future where energy  
is clean, abundant, reliable, and affordable



This presentation does not contain any proprietary, confidential, or otherwise restricted information

UNCLASSIFIED

# LANL Project Overview

## Timeline

- Project Start Date: FY07
- Project End Date: FY08
- Percent Complete: 100%

## Budget

- Total Project Funding: 500K
- Project End Date: FY2008
- Funding:
  - 2007: \$200K
  - 2008: \$300K
  - 2009: \$0K\*

## Barriers

- **Barriers Addressed**
  - *Feedstock Cost and Availability*
  - *Capital Cost and Efficiency of Biomass Gasification/Pyrolysis Technology*

## Partners

- None

*\*EERE Hydrogen Production and Delivery Budget Zeroed Out*

# LANL Project Objectives

---

## Project Objective

Develop novel low temperature chemical routes and catalysts to produce hydrogen/syngas from lignocellulosic feedstocks

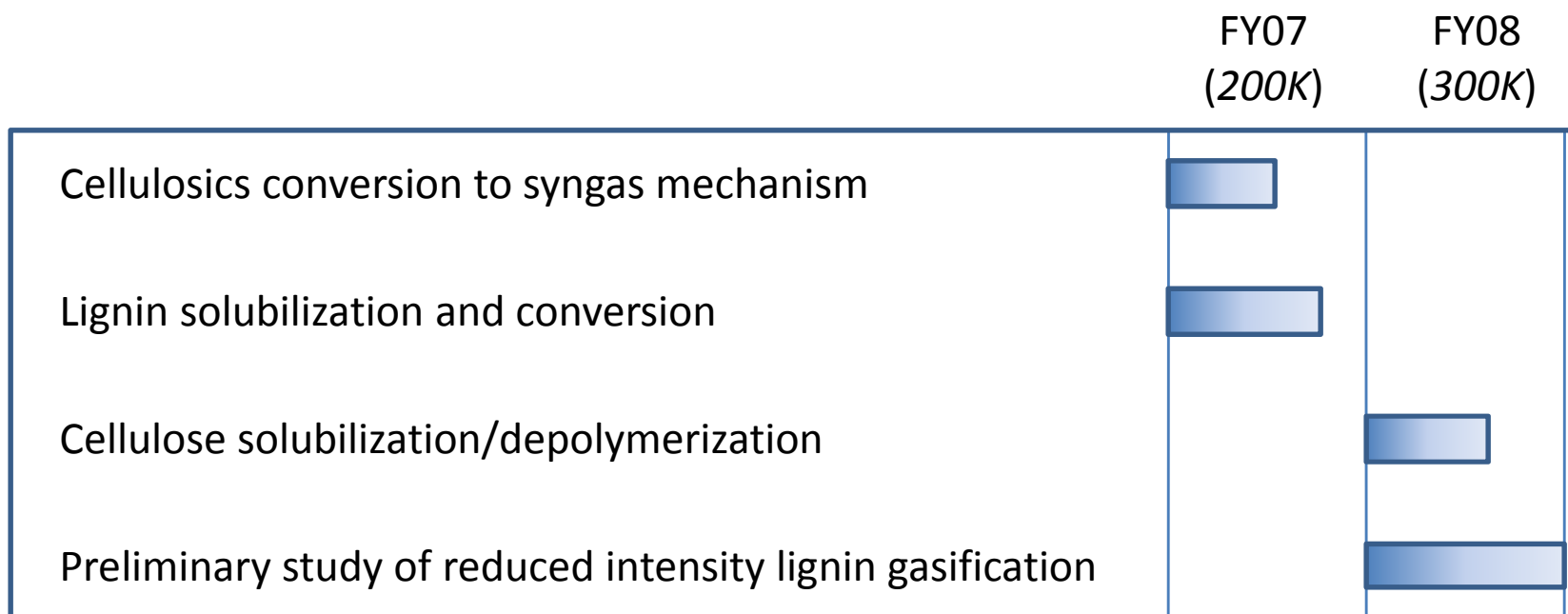
Target: By 2012, reduce the cost of hydrogen produced from biomass gasification to \$1.60/gge at the plant gate (<\$3.30/gge delivered). By 2017, reduce the cost of hydrogen produced from biomass gasification to \$1.10/gge at the plant gate (\$2.10/gge delivered).

*The most abundant constituent of biomass is lignocellulosic (~80%). Discovering new chemistries and catalysts that can convert lignocellulosic into hydrogen/syngas will be critical if biomass is to be used as a feedstock for hydrogen or other alternative fuels.*

*Lignocellulosic depolymerization/decomposition is the most process intensive (and most challenging) constituent of biomass to convert to hydrogen/syngas*

# LANL Project Milestones

## Milestones: Catalytic Solubilization and Conversion of Lignocellulosic Feedstocks



# LANL Project Approach

---

In general terms, LANL is in search of novel hydrogen/syngas production routes from lignocellulosics. Two approaches will be explored:

- Catalytic solubilization of lignocellulosics to generate a sugar feedstock stream for downstream APR, and
- Solubilization of lignocellulosics followed by APRxn of oligomeric, soluble cellulose.

LANL will conduct screening experiments for evidence of direct aqueous-phase low-temperature reforming of lignocellulosics to hydrogen/syngas through the use of catalysts designed to cleave carbon-carbon bonds of the cellulose backbone. Tandem catalysis approaches, where two catalysts or processes are linked together in a single reaction vessel, will be explored to demonstrate “one-pot” cellulose solubilization followed by aqueous phase catalytic reforming to generate hydrogen. This is important in that if catalysts can be found that will generate hydrogen directly from soluble cellulose oligomers, this provides a ‘one-pot’ approach and offers increased utilization of residual biomass, increased efficiency and the potential for cost reductions both in feedstock and in capital equipment. LANL’s approach to producing hydrogen from lignocellulosics (i.e., middle and bottom routes) is represented by the chemical routes shown in Figure 1 (next slide).

# LANL Project Approach (cont'd, Figure 1)

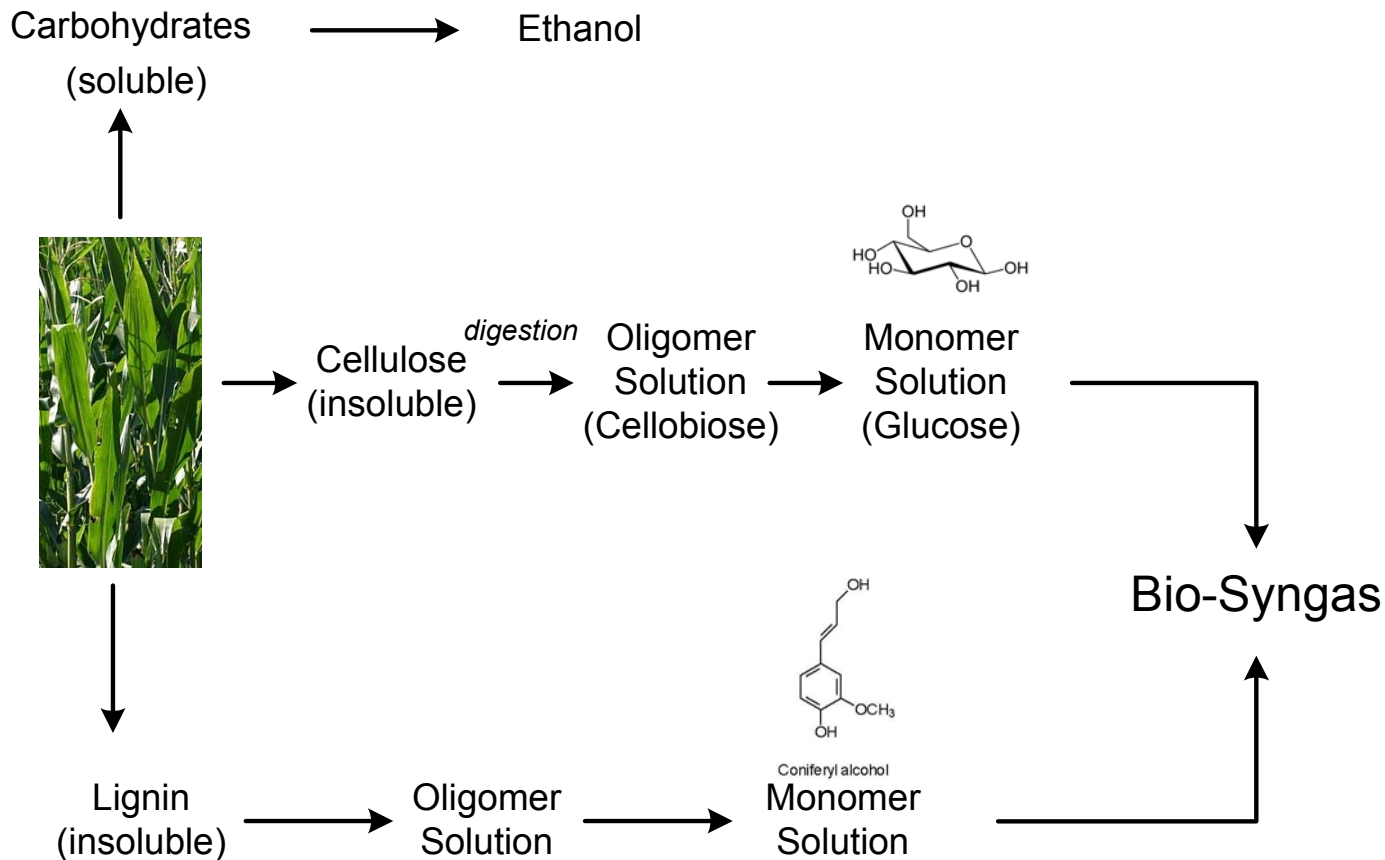


Figure 1. A rudimentary diagram showing LANL's approach to producing bio-syngas (i.e, hydrogen and carbon monoxide) from lignocellulosics

# LANL Technical Accomplishments and Progress

---

## Accomplishments

- Demonstrated heterogeneous catalyzed hydrolysis of cellobiose to glucose.
- Demonstrated the conversion of cellobiose to syngas [albeit at low conversions (~5%)]
- Demonstrated catalytically enhanced decarboxylation of lignin.
- Performed baseline characterization studies on model compounds (i.e., lignin and cellobiose)
- Demonstrated low temperature catalyzed gasification of lignin

# LANL Overview of Scoping Experiments

---

- Flow reactor system for liquid conversion (bench-scale)
- Batch reactors for liquid/solid conversion (bench-scale)
- Scoping experimental results
  - Liquid phase conversion
    - (Glucose, Cellobiose)
  - Solid phase mass conversion
    - (Lignin, Pine)
  - Residual solids analysis
    - TGA (thermal gravimetric analysis)
    - NMR
    - FTIR (molecular vibrational frequencies)
  - Product analysis
    - LC (liquid chromatograph)
    - Gas Analysis

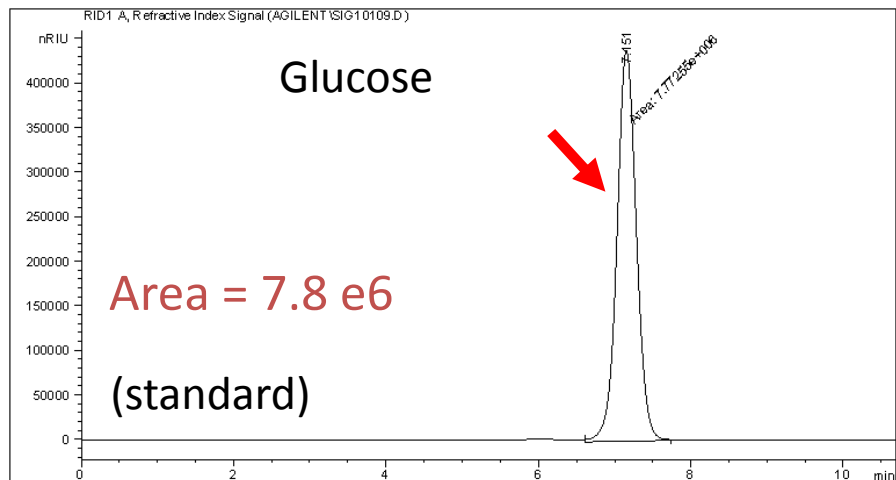


# Conversion of Liquid Phase

---

- Heterogeneous catalytic conversion of soluble phase
  - Glucose and Cellobiose to vapor phase products
- Homogeneous catalytic conversion of model cellulose
  - Cellobiose as model compound to demonstrate solubization
- Operation
  - Flow reactor
    - Well defined conditions (control of T, P, flows)
    - Gas analysis
  - Batch reactors – closed system
    - Reactants loaded, put in oven
      - T = 100 – 275 °C; 4 – 18 hrs
    - Post analysis
  - Catalysts
    - Base metals, noble metals with Lewis acid supports (Al<sub>2</sub>O<sub>3</sub>, zeolites)
    - Ln Triflates, perfluorosulphonic acid as homogeneous Lewis acids

# Liquid Chromatography Analysis



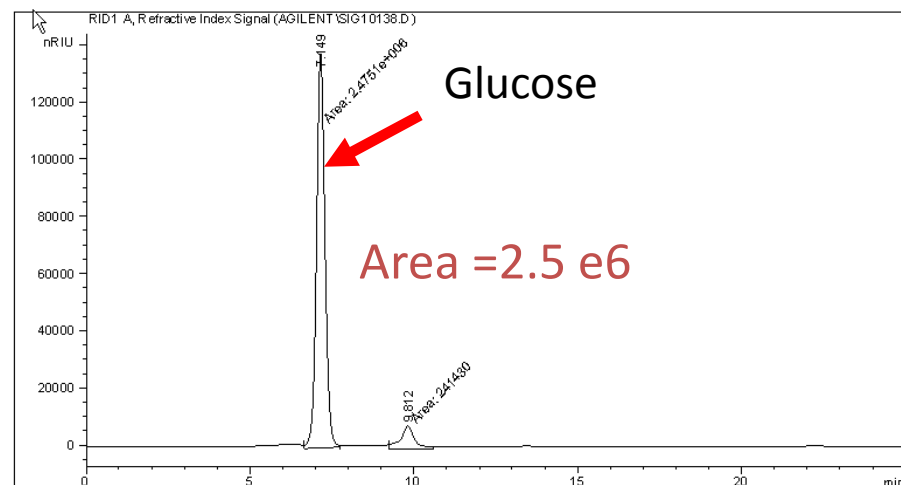
← Different Scale →

Reactant: Glucose Catalyst: Pt

Batch Reactor Conditions:

$T_{rxn} = 100\text{ }^{\circ}\text{C}$ ,  $t_{rxn} = 18\text{ hrs}$

Conversion:  $\sim 68\%$



Observations:

- Unidentified liquid phase products (trace)
- Products primarily in vapor phase

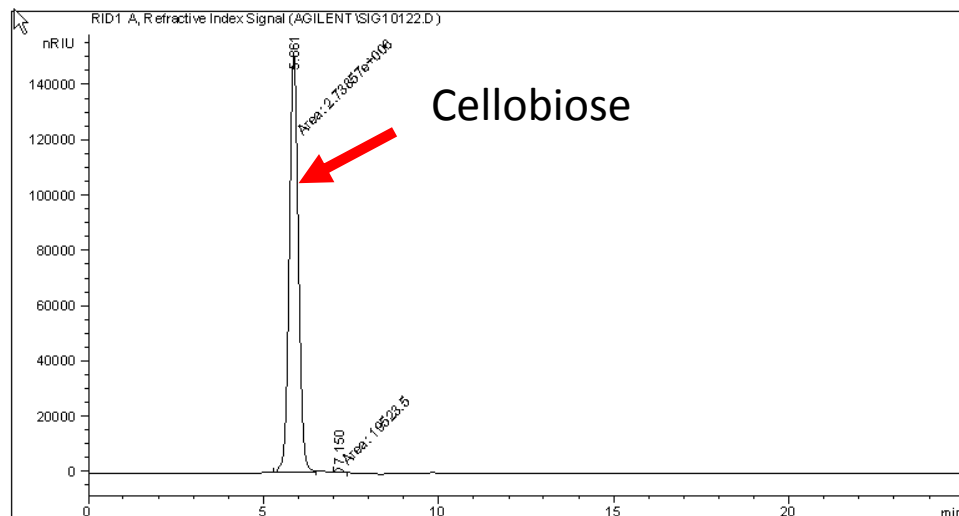
# Liquid Chromatography Analysis (cont'd)

Reactant: **Cellobiose**      Catalyst: **None**

Batch Reactor Conditions:

$T_{rxn} = 100\text{ }^{\circ}\text{C}$ ,  $t_{rxn} = 18\text{ hrs}$

Conversion:  $\sim 13.8\%$



Reactant: **Cellobiose**      Catalyst: **Pt/Rh**

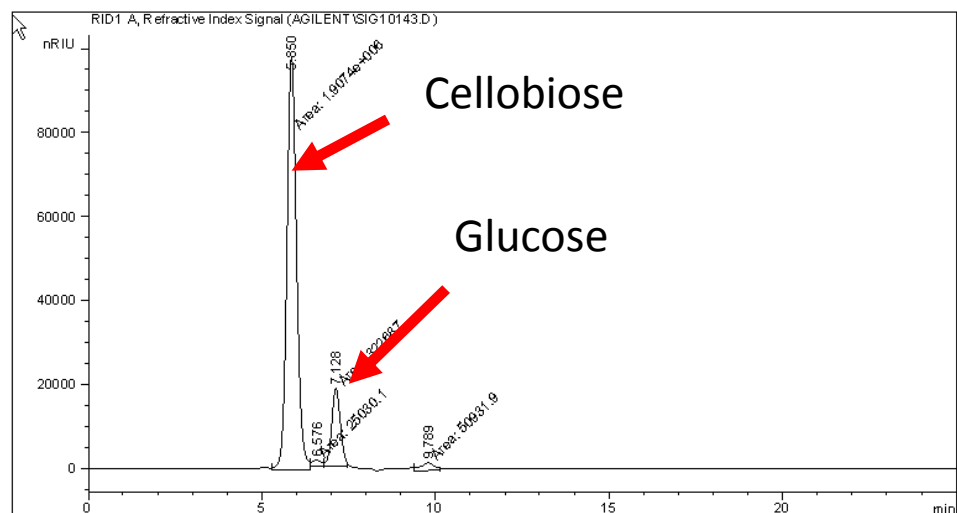
Batch Reactor Conditions:

$T_{rxn} = 100\text{ }^{\circ}\text{C}$ ,  $t_{rxn} = 18\text{ hrs}$

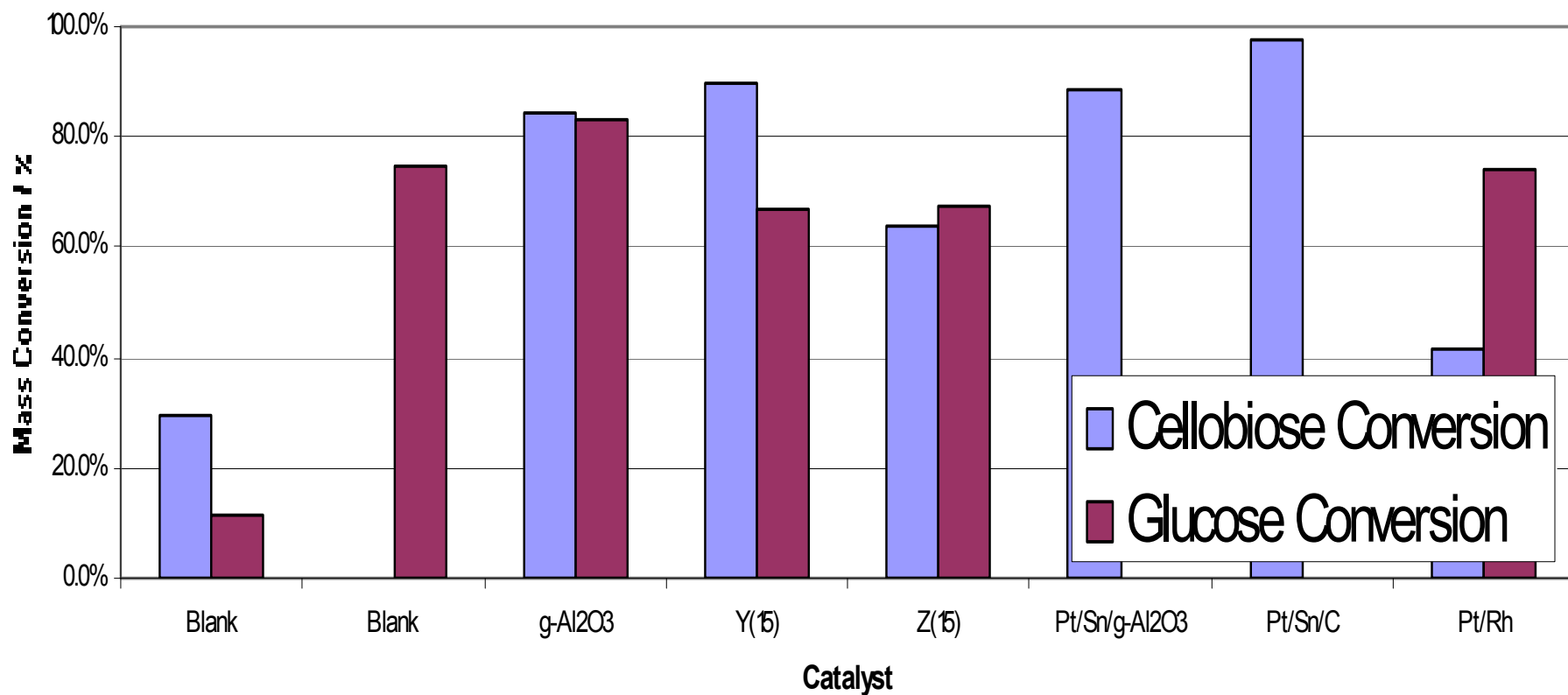
Conversion:  $\sim 42\%$

Observations:

- Unidentified liquid phase products (trace)
- Products primarily in vapor phase



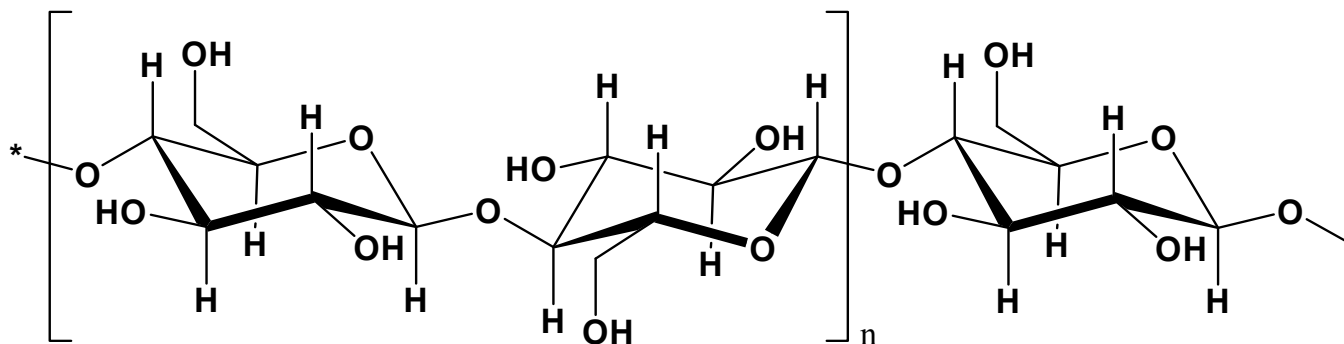
# Liquid Phase Reactant Conversion



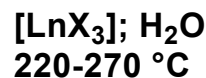
Liquid analysis indicates heterogeneous conversion of Glucose and Cellobiose

# Digestion of Cellulose with $\text{LnX}_3$

Can Lanthanide Salts  $\text{LnX}_3$  ( $\text{X} = \text{OTf}, \text{Cl}$ ) act as hydrolysis catalyst?



microcrystalline cellulose



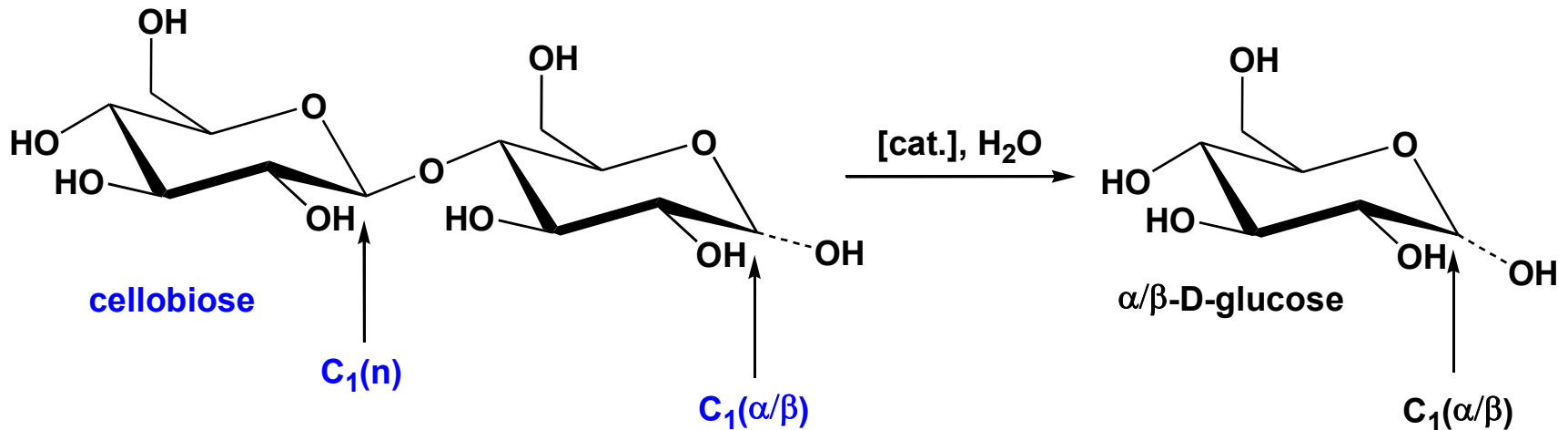
water and methanol soluble components (oligosaccharides ?)  
in up to 50 % yield - no further characterization or analysis



Literature search reveals a single study by Japanese researchers:

T. Sakaki et al., Jpn. Kokai Tokkyo Koho, **2002**, Jap. Pat. 2002085100; CAN 136:246813

# Cellobiose as a Model for Cellulose

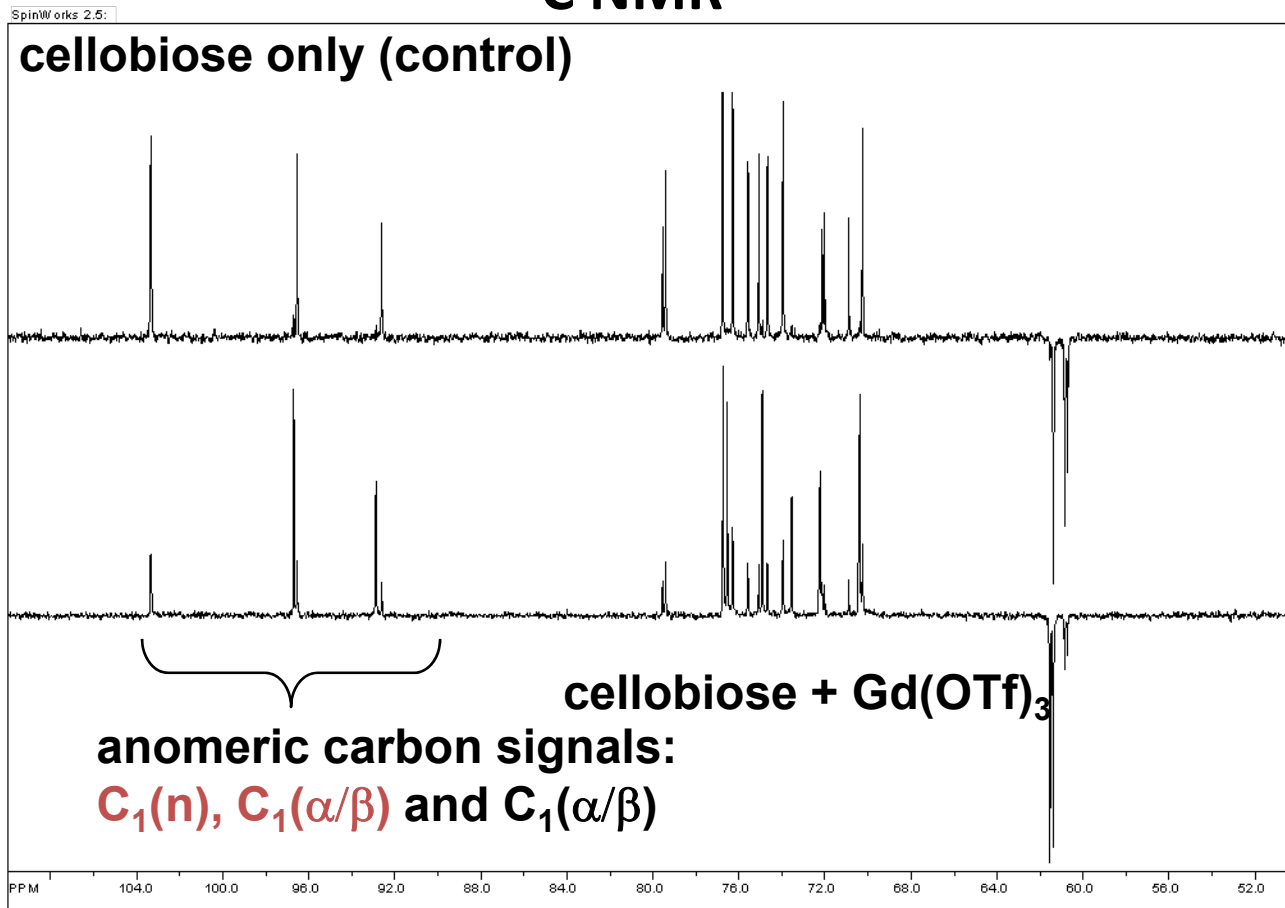


## NMR Analysis

- Anomeric carbons  $C_1$  and their associated protons give distinct and easily tracked resonances in the  $^{13}C$  and  $^1H$  NMR.
- Expect 3 signals for cellobiose:  $n$ ,  $\alpha$  &  $\beta$
- Expect 2 slightly shifted signals for glucose:  $\alpha$  &  $\beta$

# Catalyzed Hydrolysis of Cellobiose to Glucose

## $^{13}\text{C}$ NMR

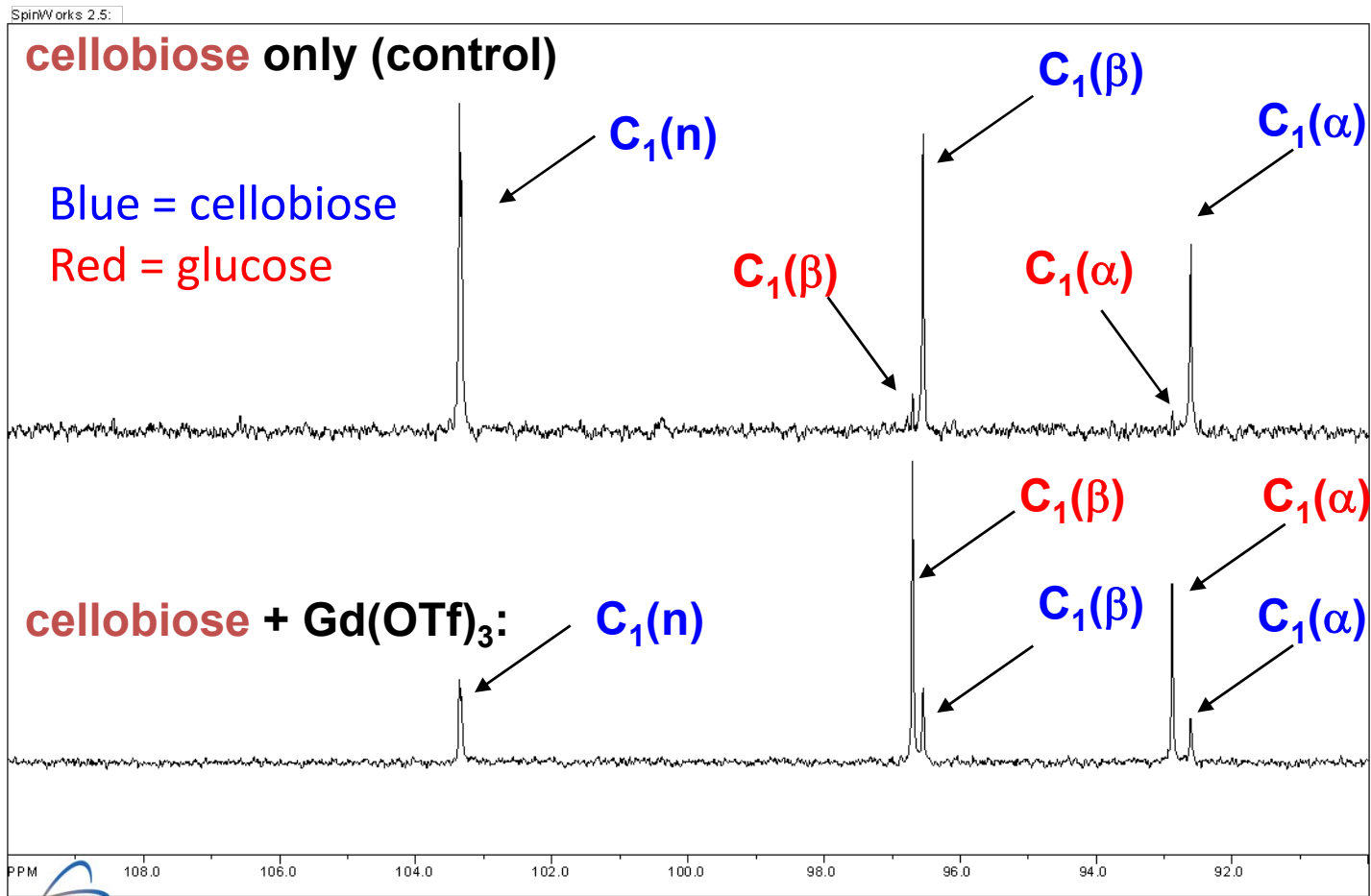


Next Slide:  
Compare  
anomeric carbon  
signals

$\text{Gd}(\text{OTf})_3$  (1 mol%)  
Cellobiose (0.33 mol/L in water)  
(120 °C for 13 h)

# Catalyzed Hydrolysis of Cellobiose to Glucose

## $^{13}\text{C}$ NMR Anomeric Carbon Signals Magnified



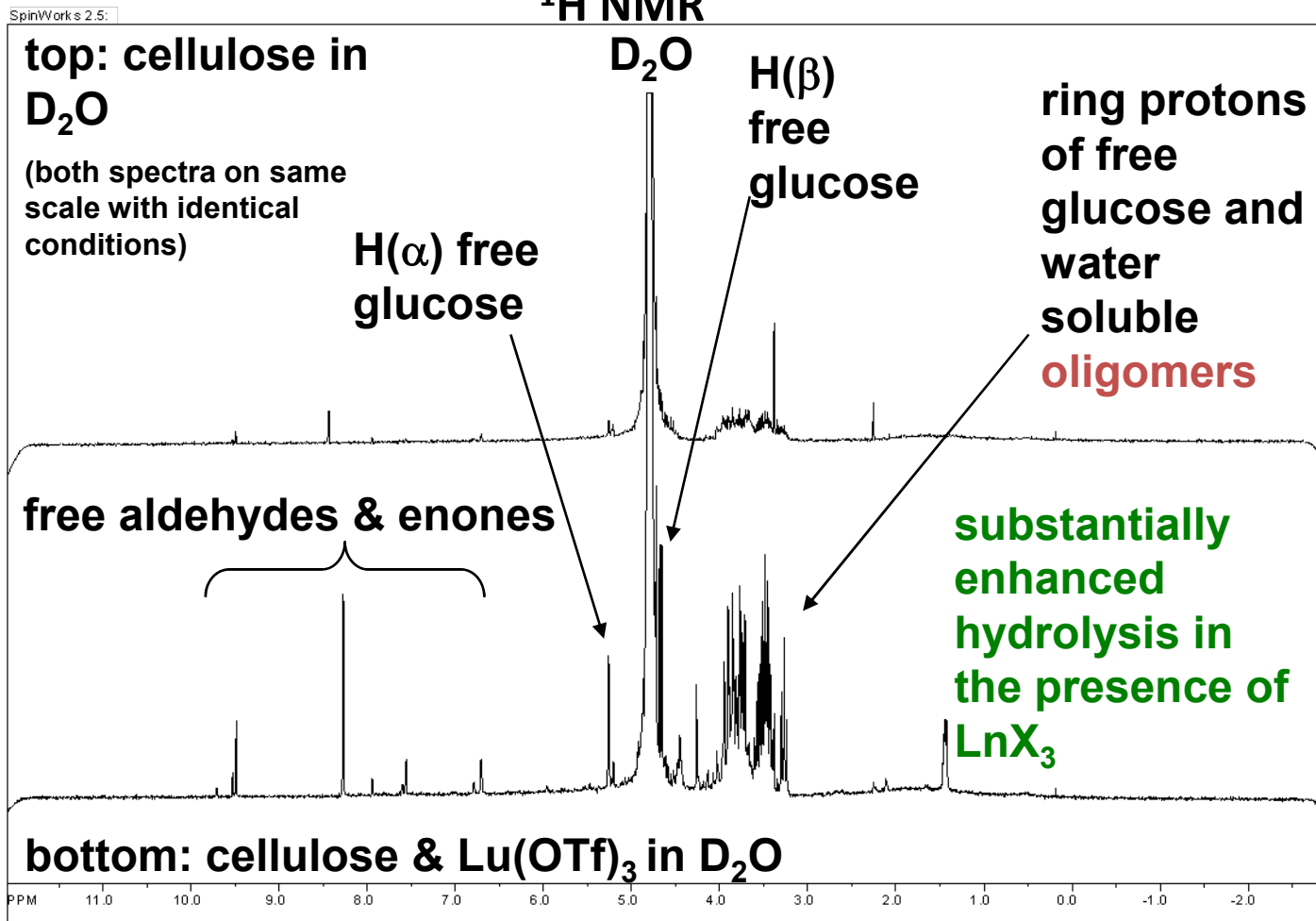
< 5 % conversion  
to free glucose

~ 75 % conversion  
to free glucose  
without significant  
decomposition



# Catalyzed Hydrolysis of Cellulose (Aqueous Suspension)

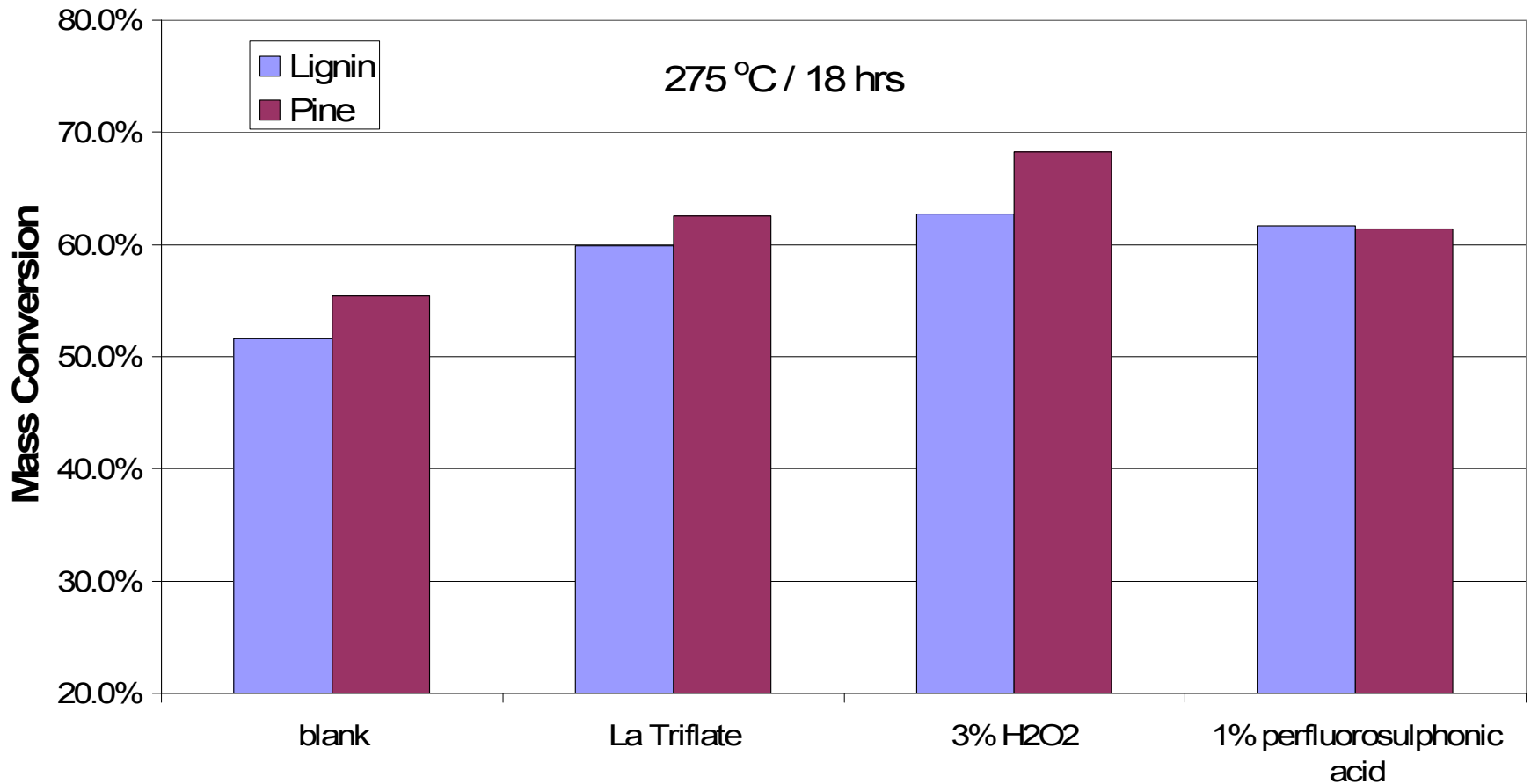
## $^1\text{H}$ NMR



Lewis acid catalysis shows hydrolysis of cellulose

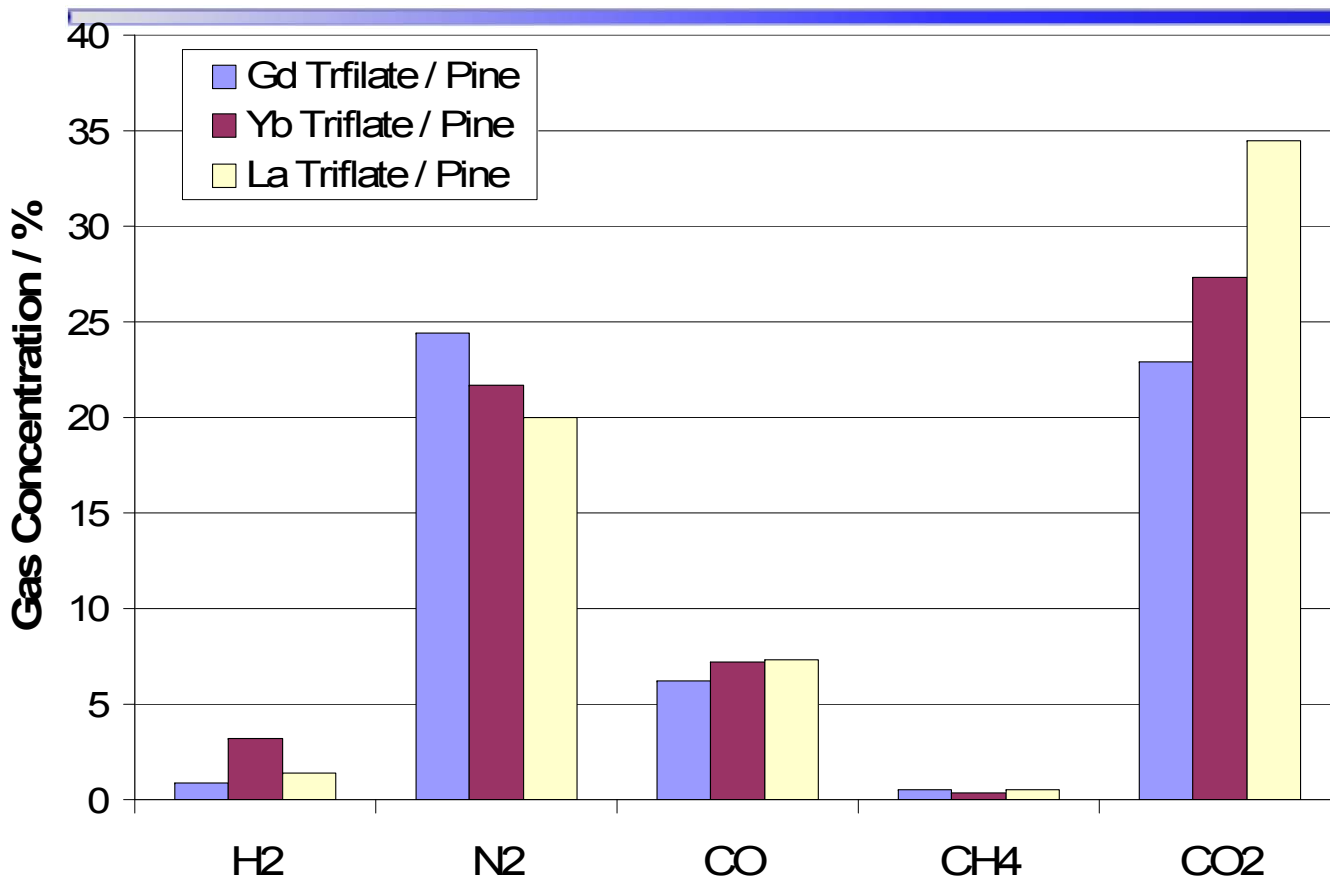
Cellobiose is good model compound

# Solid Phase Conversion of Lignin



Enhanced catalytic conversion of solids, But rates too slow

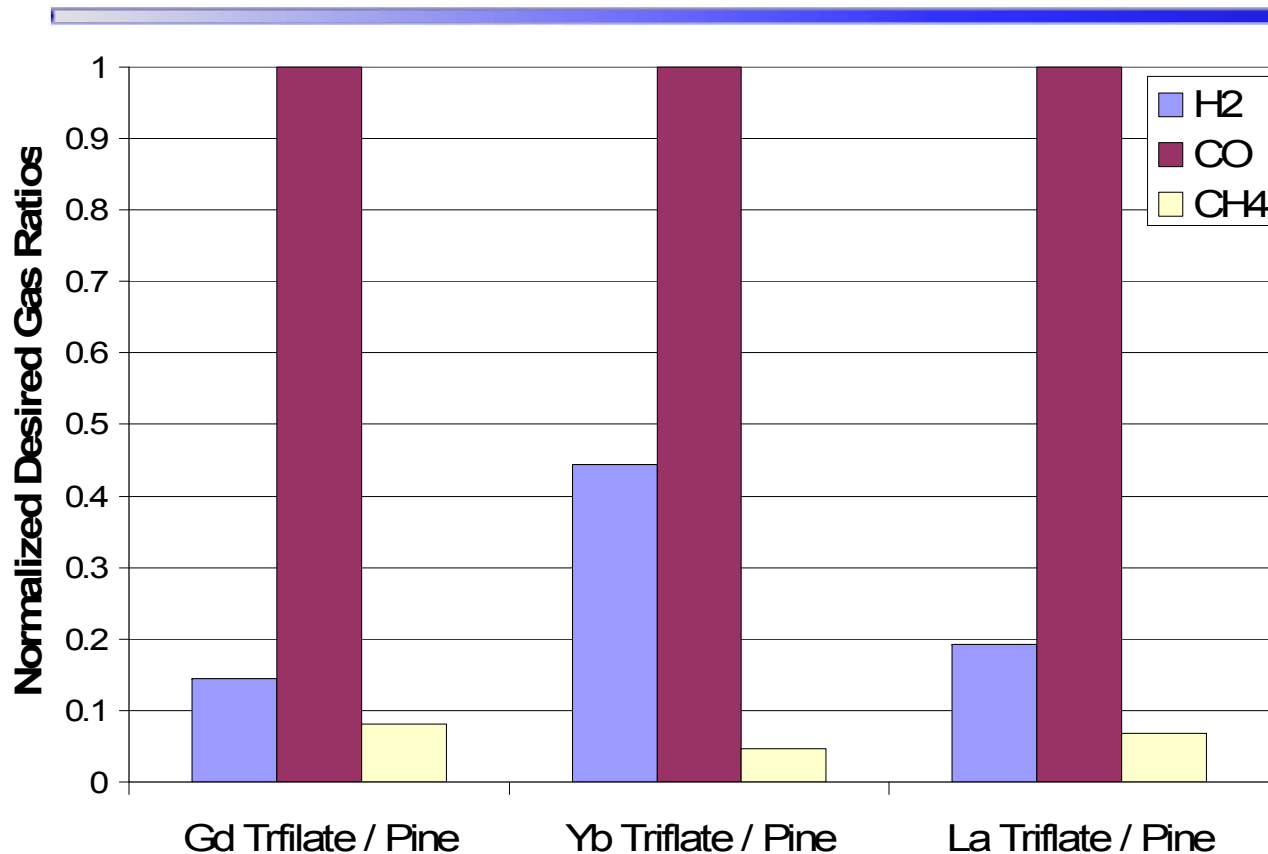
# Lignin Gasification Product Distribution



Batch Operation: Pine  
Treatment @ 225°C for  
18 hrs

Gas Analysis post batch reactor operation  
N<sub>2</sub> from air in overhead reactor space

# Lignin Gas Phase Product Ratios



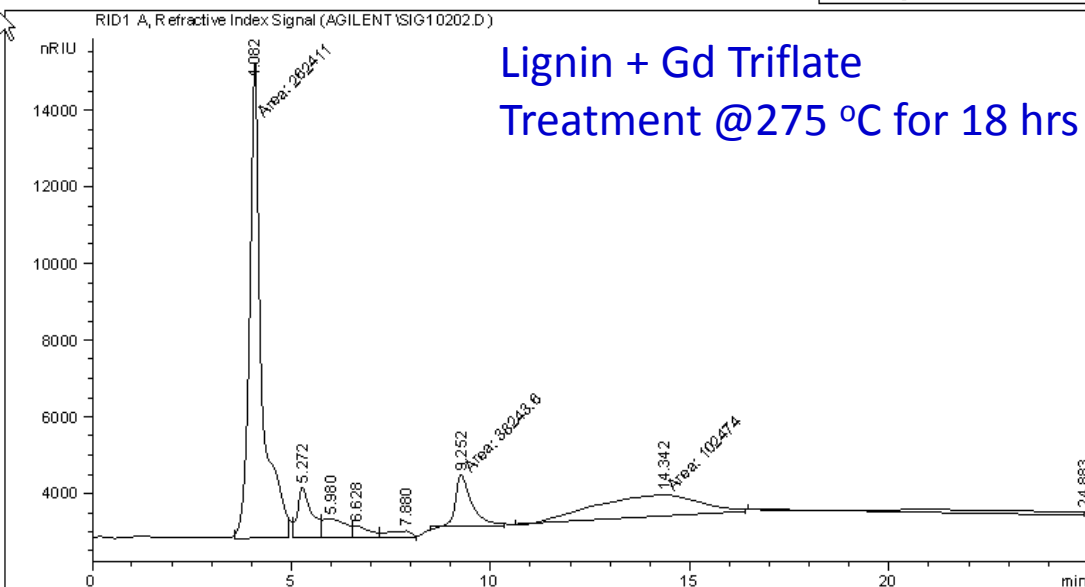
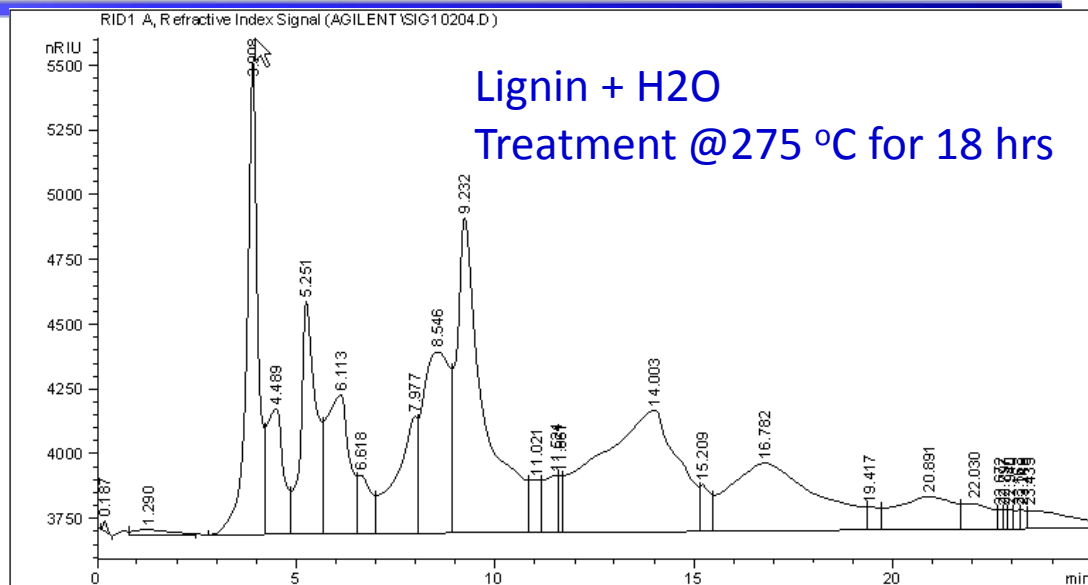
Should have ~  
equilibrium via W.G.S.  
reaction between  $H_2$ , CO,  
 $CO_2$ ,  $H_2O$   
Likely losing  $H_2$  via  
reactor septum

Desired products:

$CO > H_2 > CH_4$

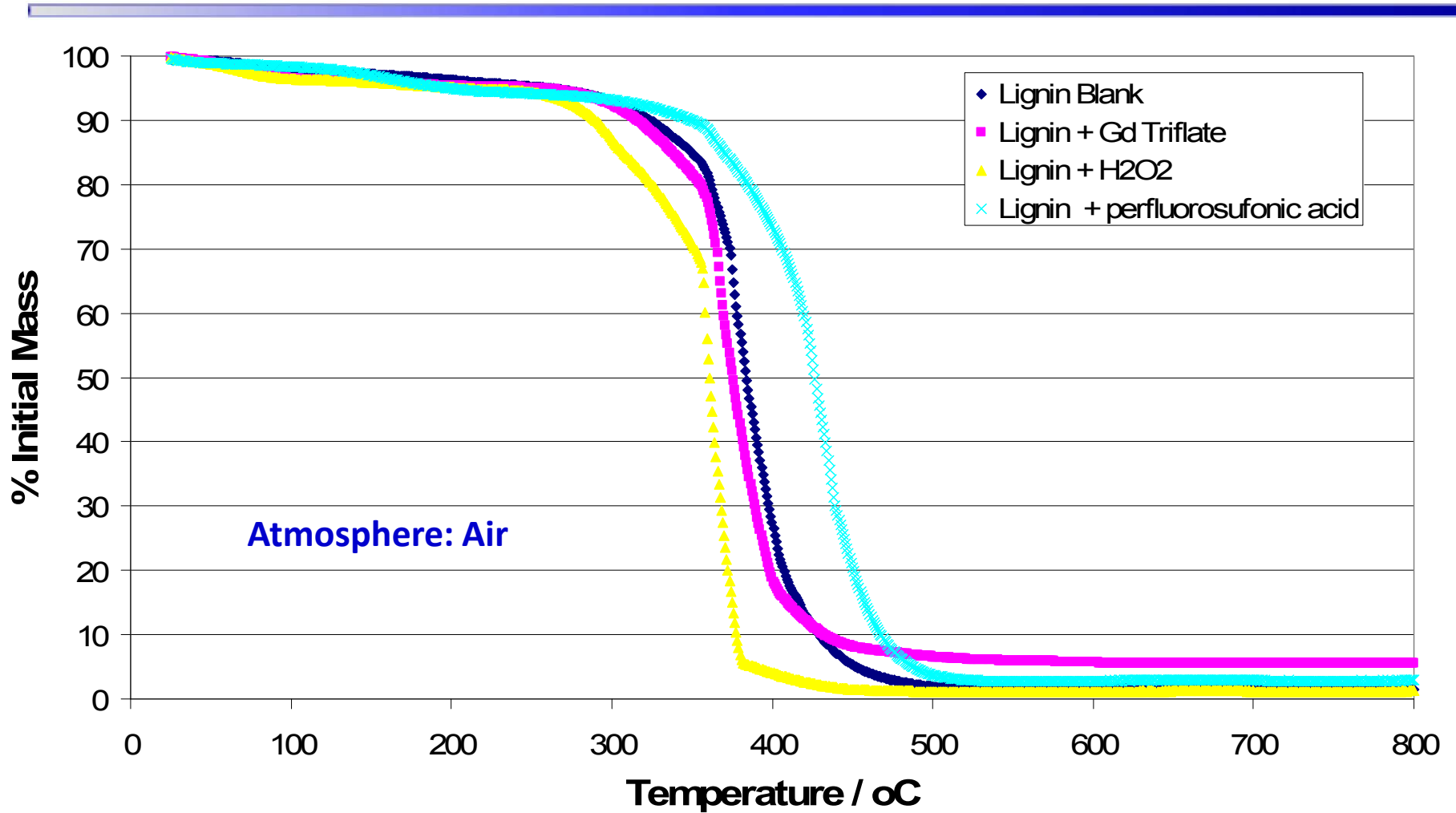
Major products are not alkanes

# Liquid Analysis of Lignin products

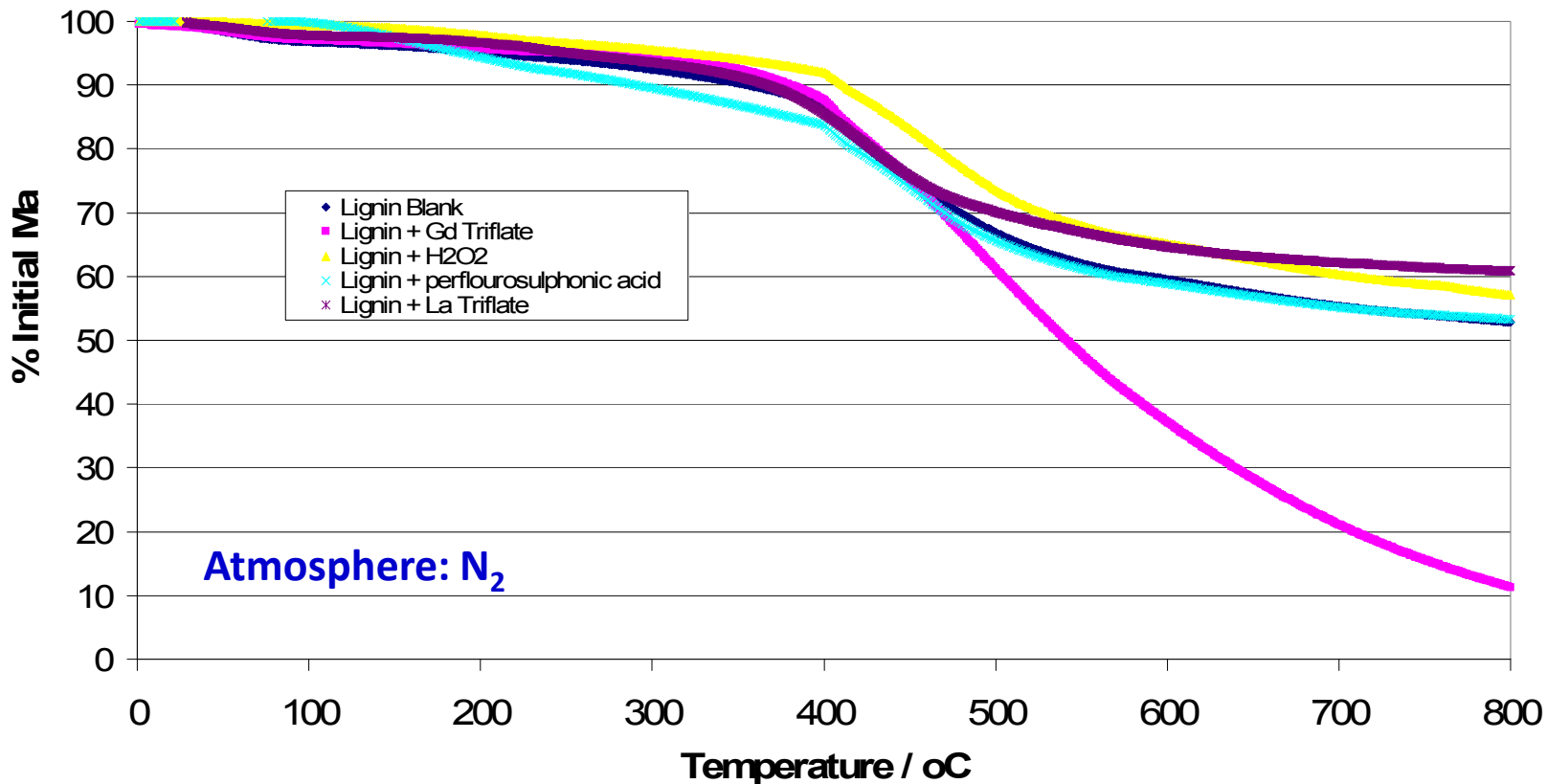


Significant reduction in higher residence time species when catalyzed by Gd Triflate

# TGA of Lignin Residue After Various Treatments

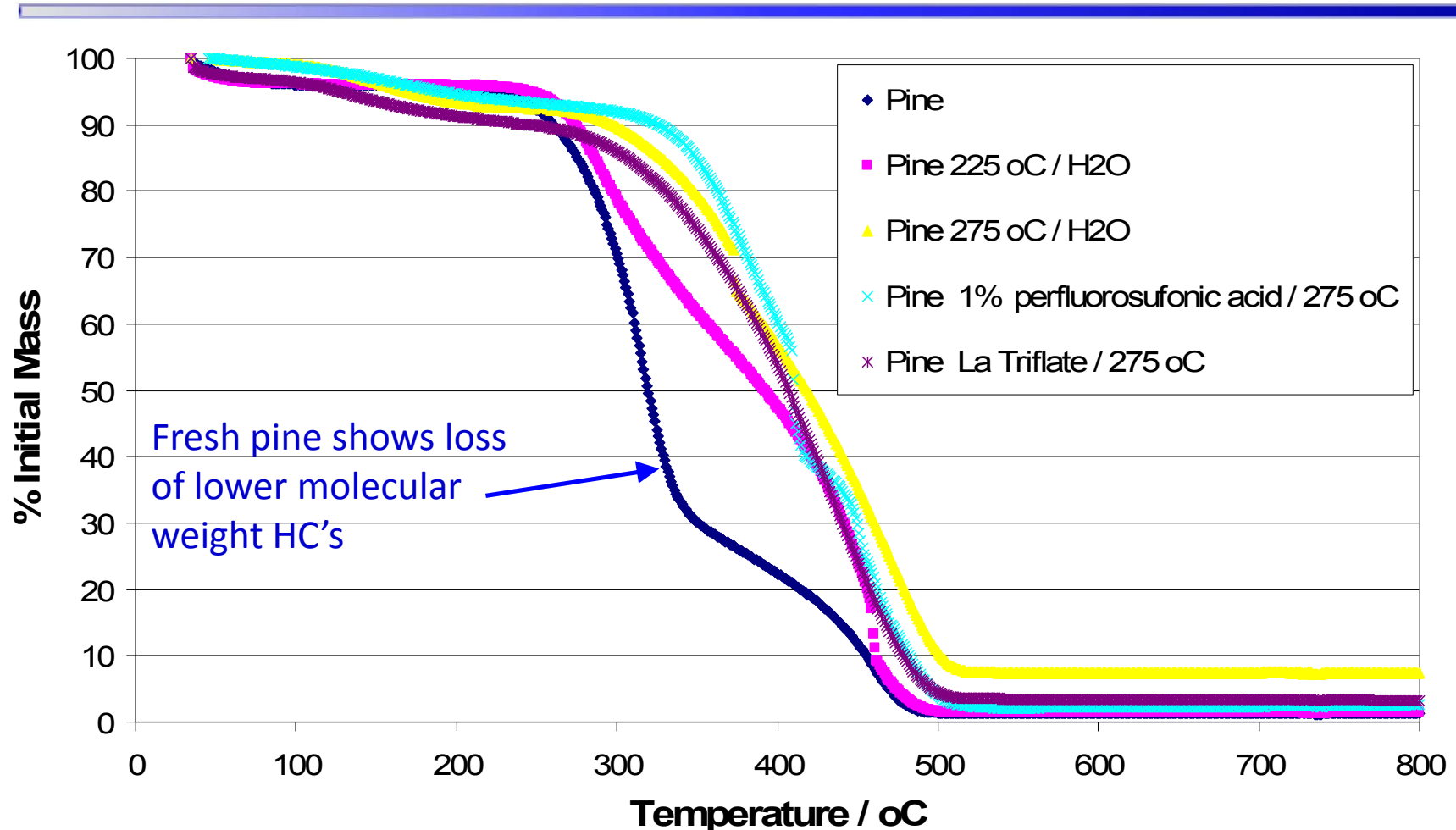


# TGA of Lignin Residue after Various Treatments



- Decomposition of Lignin
  - Most cases unchanged
  - via a different mechanism for Lignin + Gd Triflate

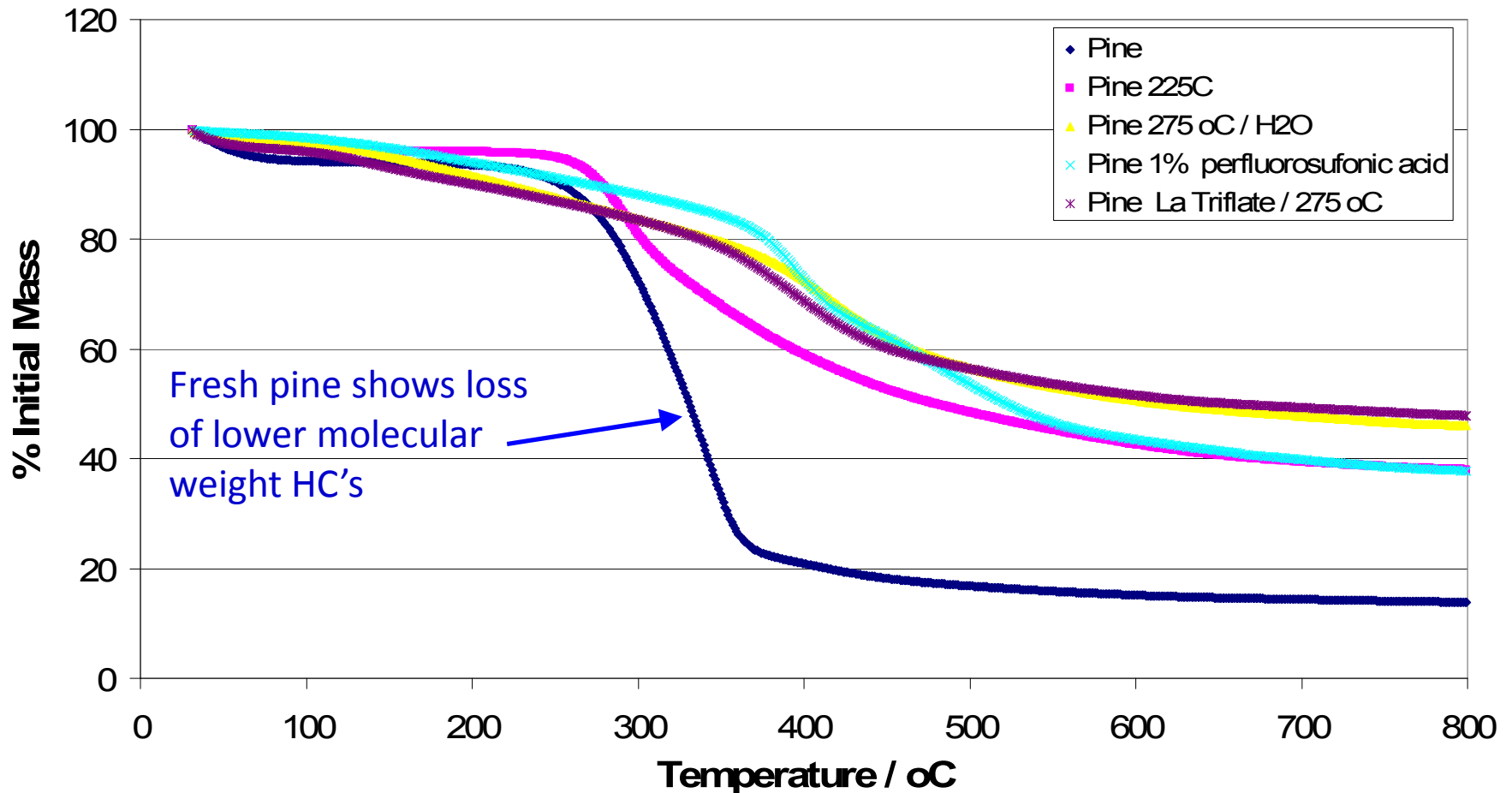
# TGA of pine in an Oxidizing Atmosphere (Air)



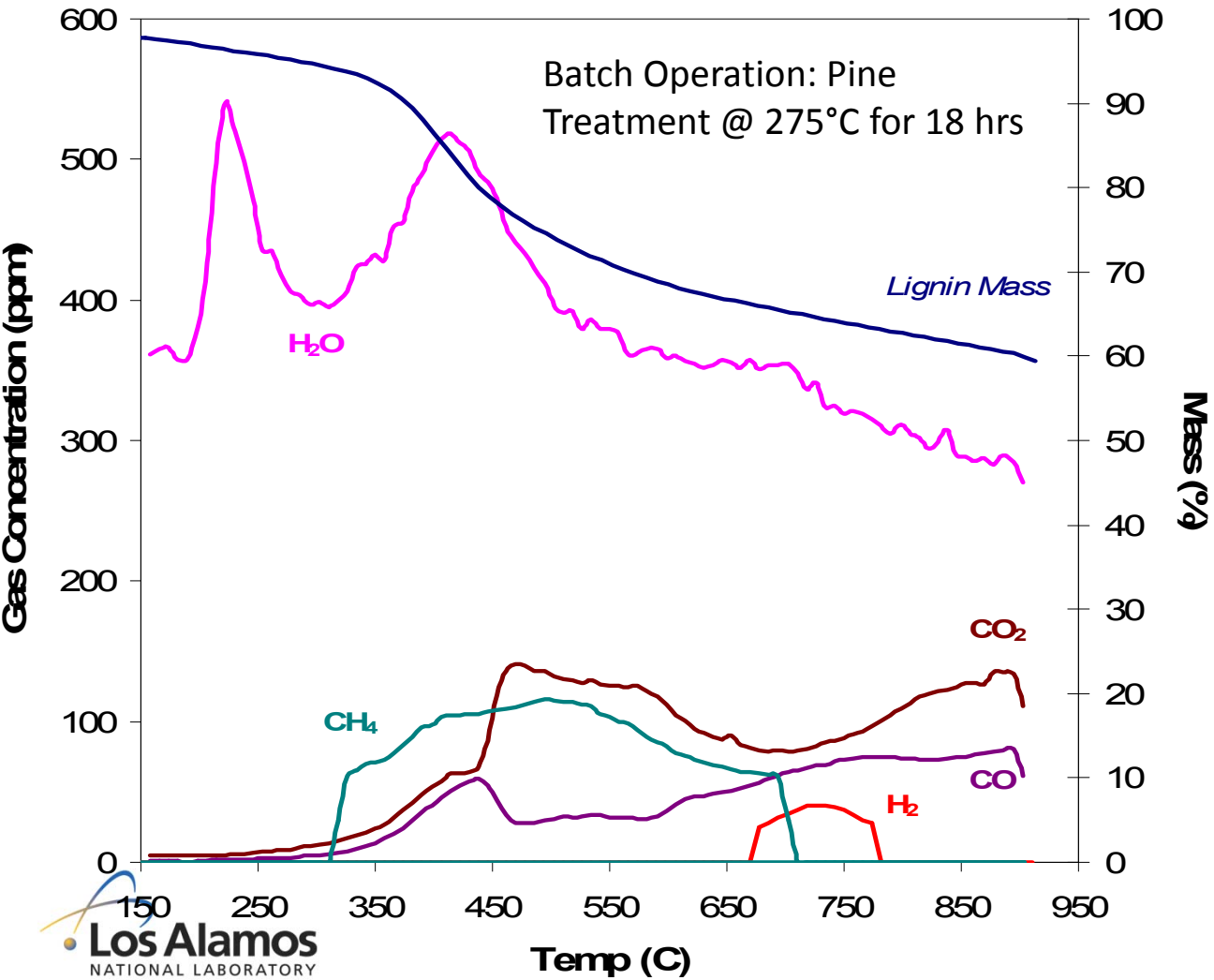
Oxidation of treated pine remains unchanged



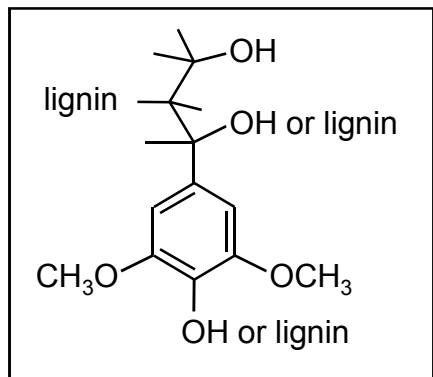
# TGA of Pine in inert atmosphere ( $N_2$ )



# TGA and Evolved Gas Analysis: Lignin Treated with Yb Triflate

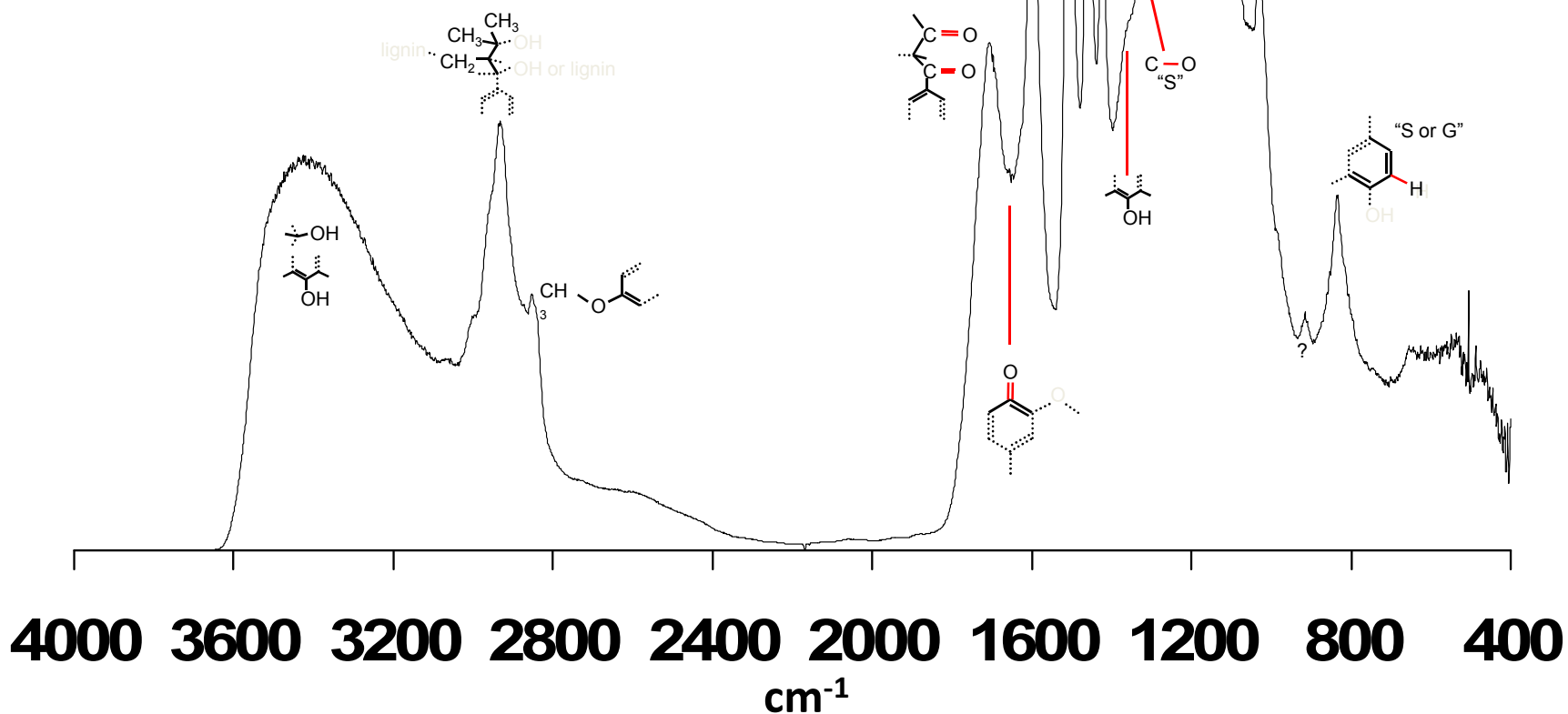


No evolution of higher molecular weight compounds

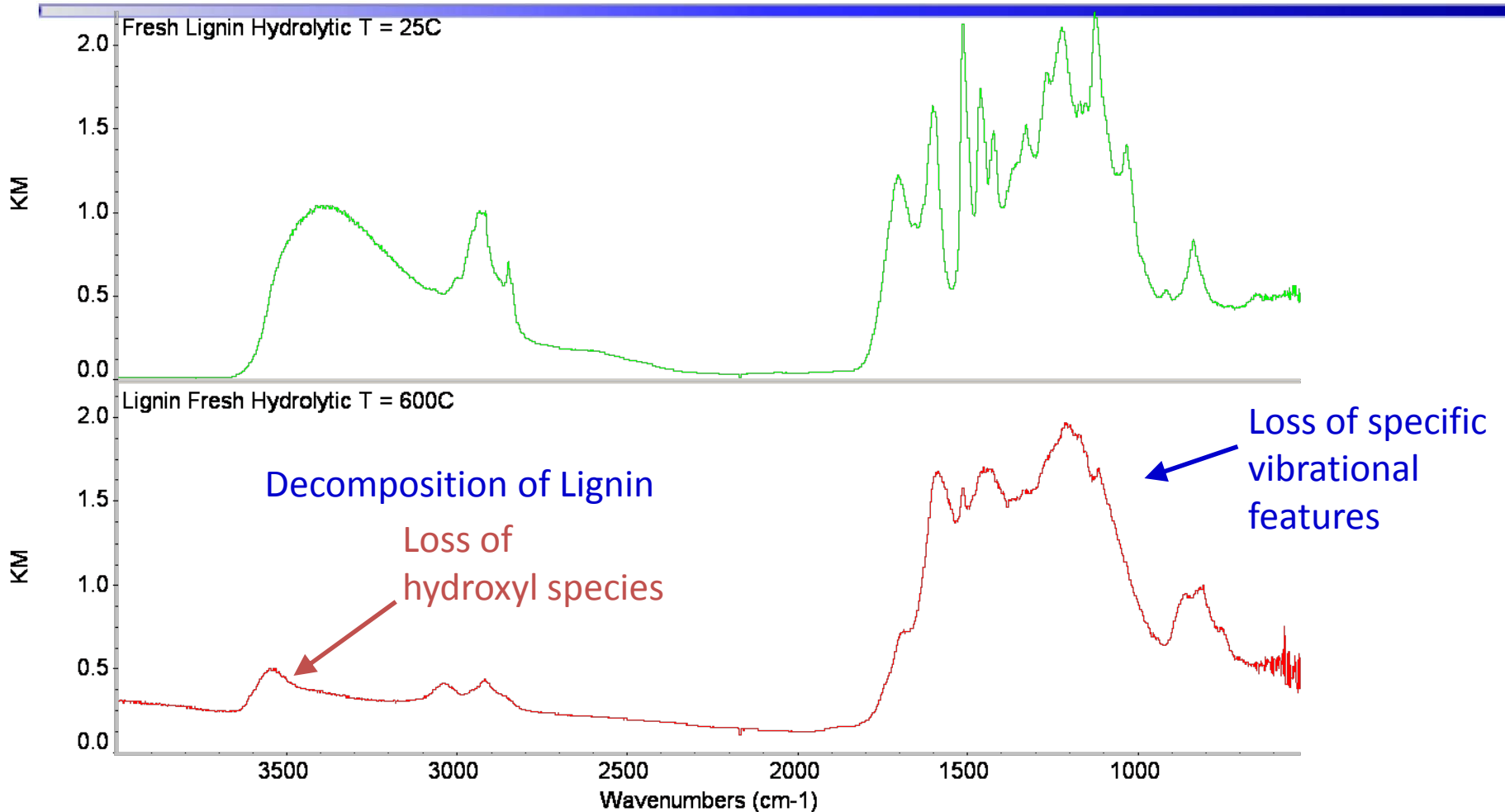


# DRIFTS: Fresh Lignin

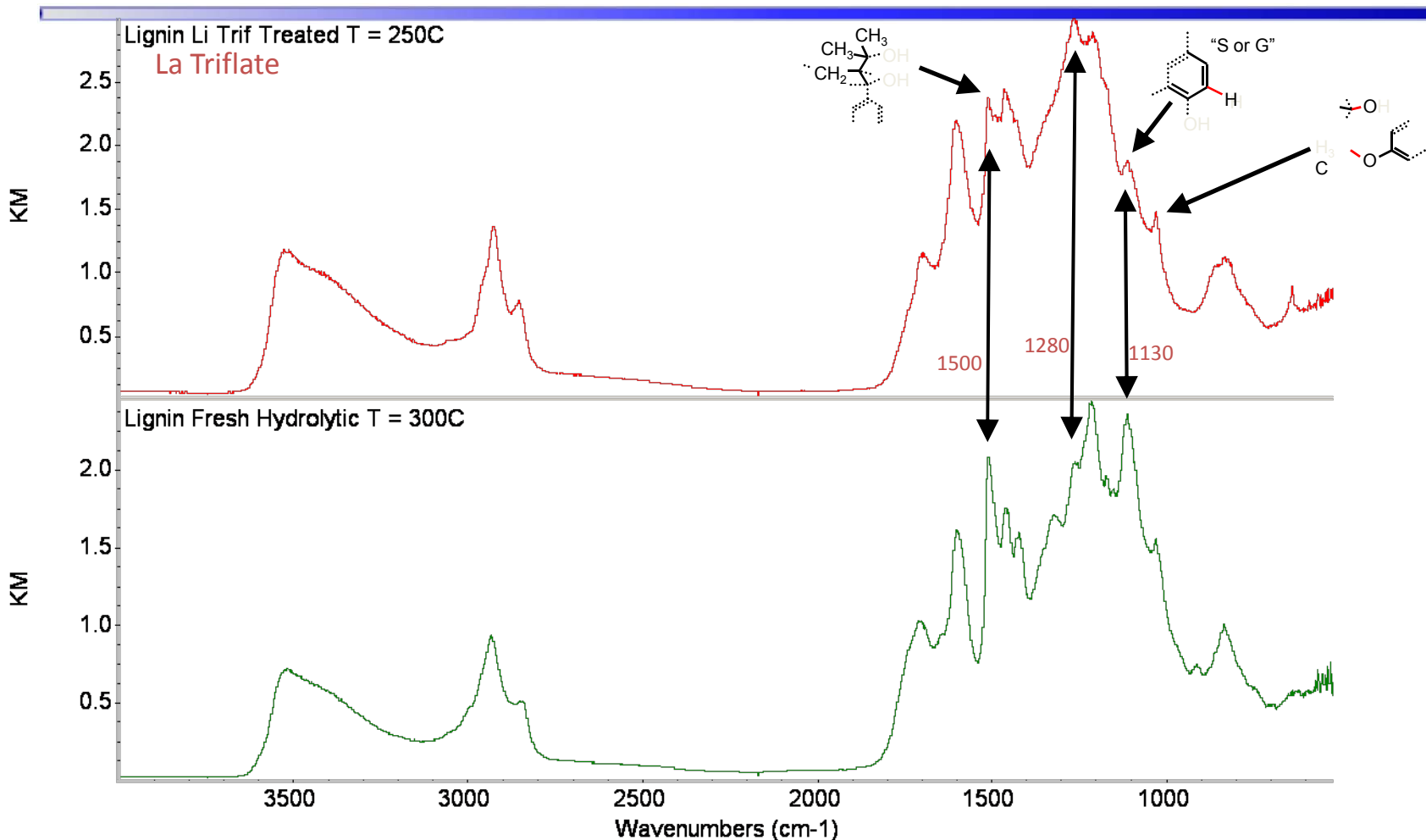
DRIFTS: Diffuse Reflectance Infrared  
Fourier Transform Spectroscopy



# DRIFTS of Lignin with Decomposition



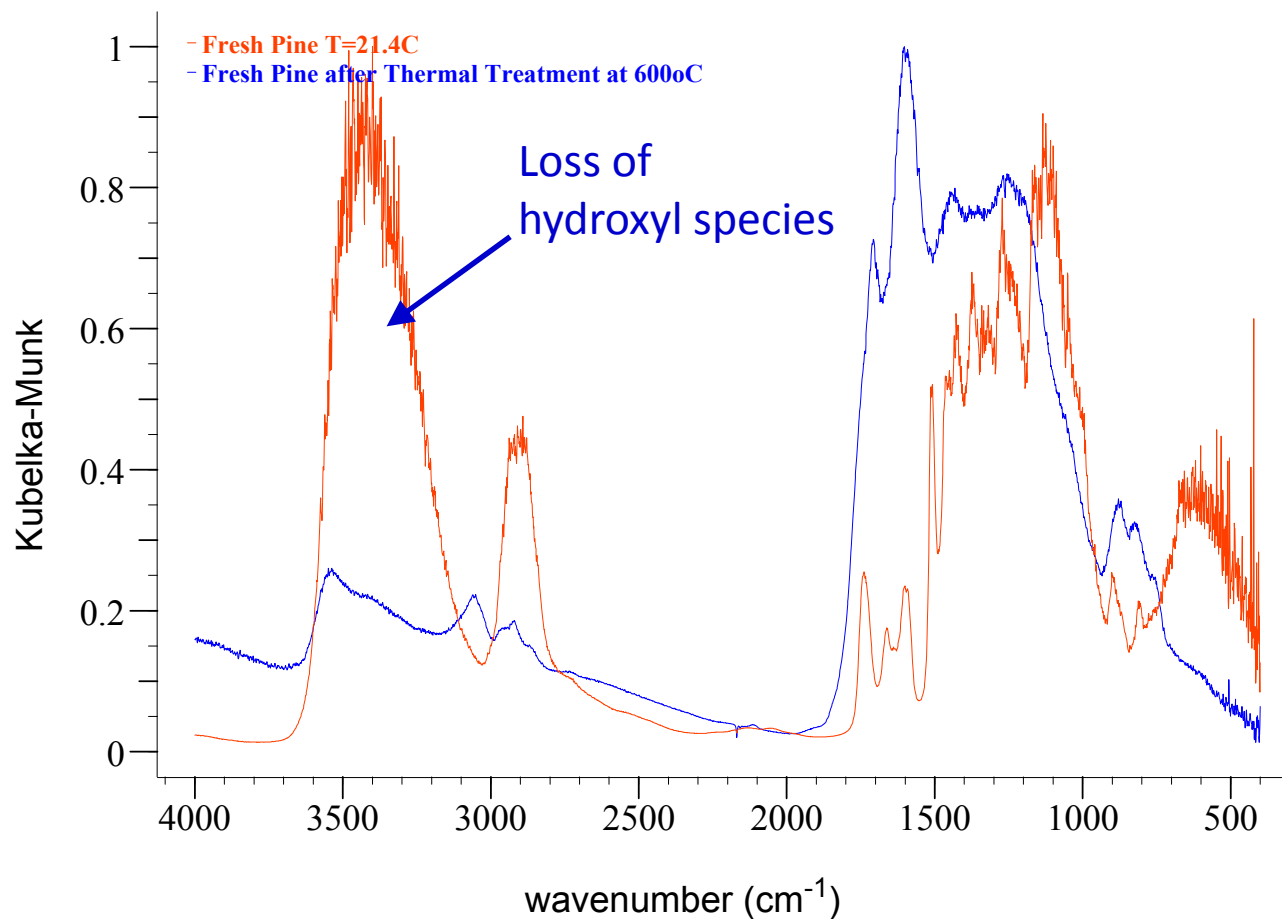
# Comparison of Fresh and Treated Lignin (300 °C)



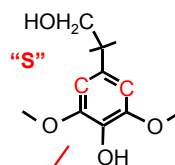
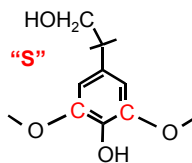
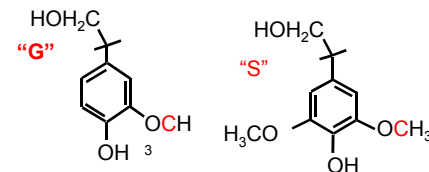
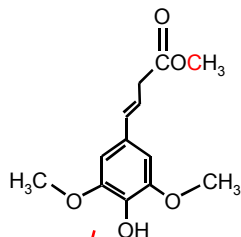
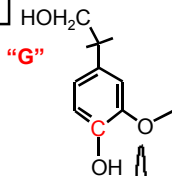
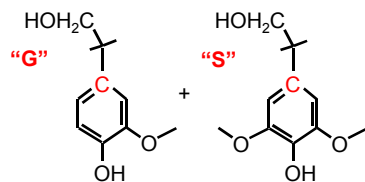
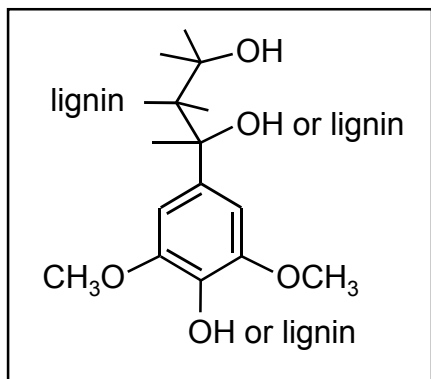
Fresh and treated lignin (300 °C)

Change in relative quantities of functionalities

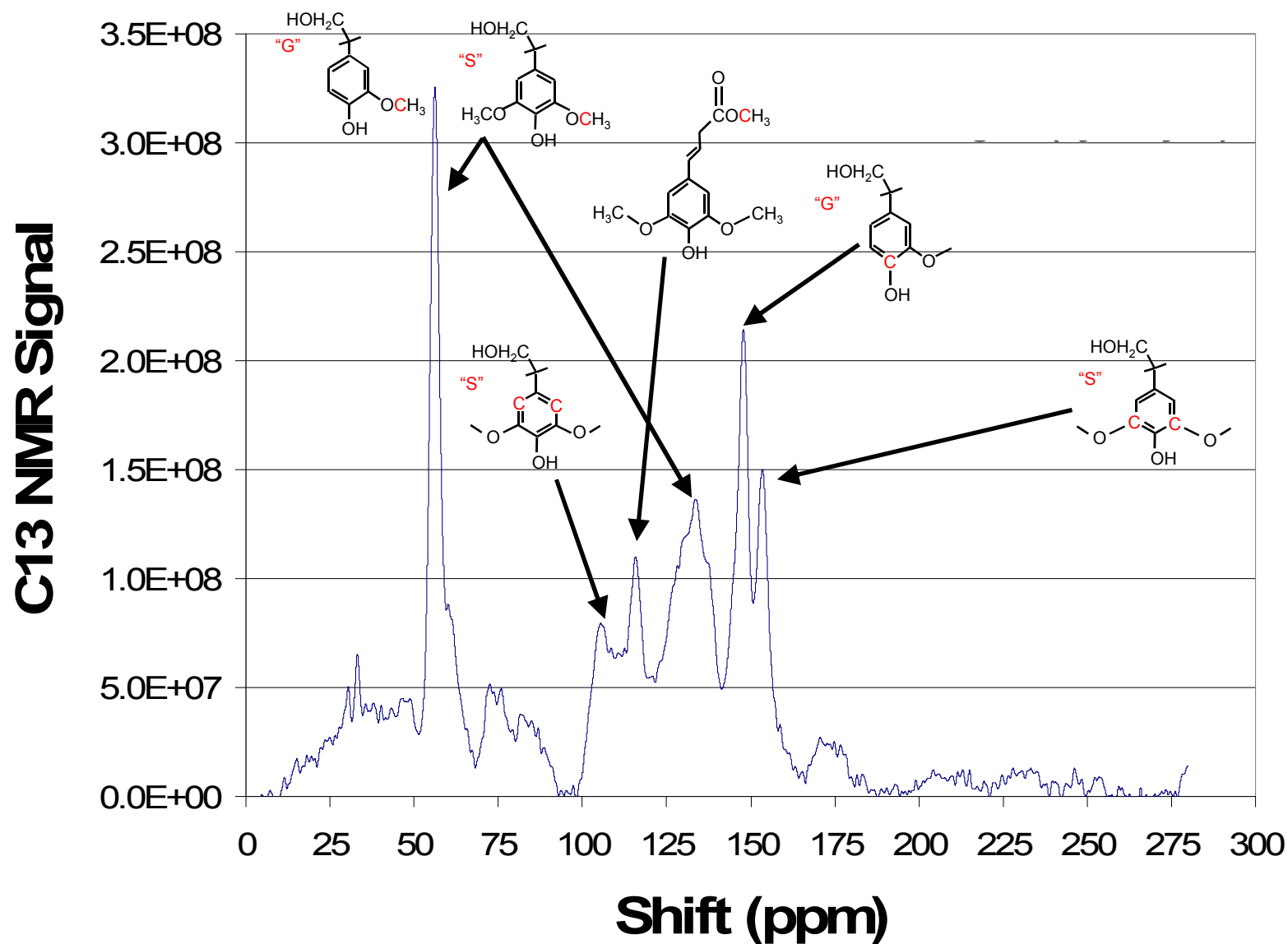
# DRIFTS of Fresh Pine and Thermally Treated



# SS-NMR of Fresh Lignin



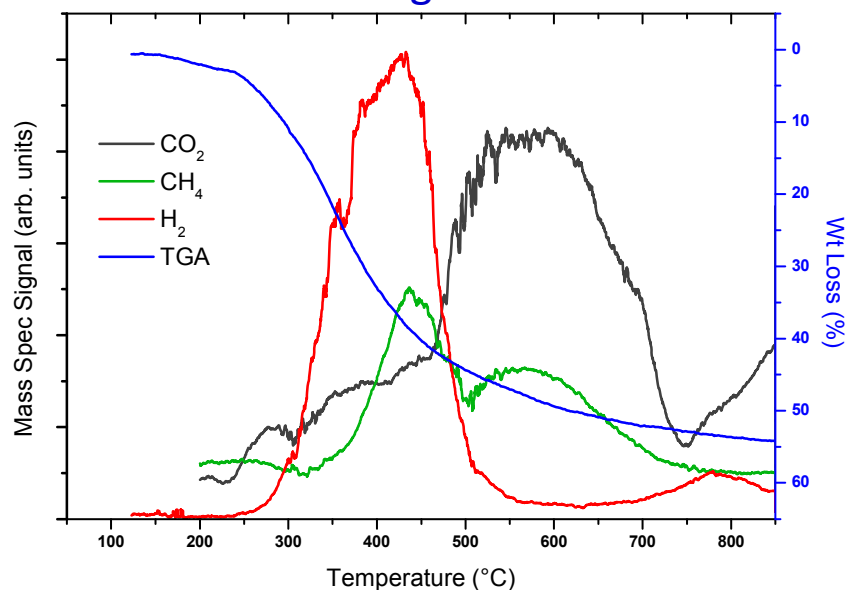
# C<sup>13</sup> SS-NMR of Fresh Lignin





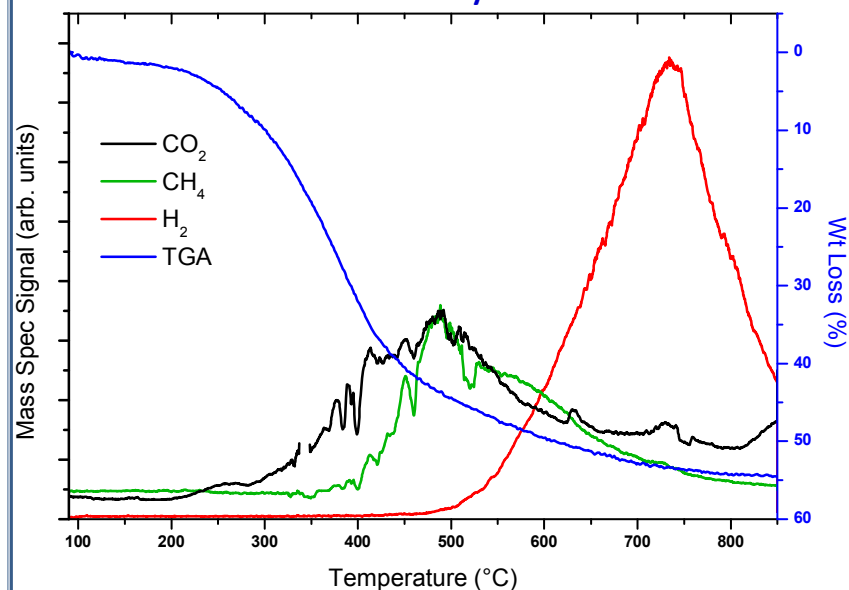
# Low Temperature Catalytic Pyrolysis/Gasification of Lignin

## Low-temperature, catalytic pyrolysis of lignin



( $T_{\text{ramp rate}} = 5^\circ\text{C}/\text{min}$ ,  $\text{N}_2$  purge rate = 30 ml/min)

## Lignin pyrolysis in the absence of a catalyst



( $T_{\text{ramp rate}} = 5^\circ\text{C}/\text{min}$ ,  $\text{N}_2$  purge rate = 30 ml/min)

Catalysts show a reduction in temperature required for hydrogen production (reduce the activation energy for the reaction)

# LANL Project Summary

---

- Conversion of cellobiose to glucose is feasible, but rates currently too low
- Lignin hydrophobicity is a critical challenge for APRxn processes
- Recent results of low temperature catalyzed pyrolysis of lignin shows potential
  - Mechanism of the low temperature catalyzed pyrolysis of lignin currently unknown
- Heterogeneous catalysis of glucose and cellobiose
  - Relatively high conversions during batch reaction (~60 – 90%)
  - Major products appear to be gas phase for heterogeneous catalysis
- Homogeneous catalysis of cellobiose hydrolysis to glucose without significant decomposition and/or caramelization
  - Aqueous cellulose suspension marginally hydrolyzed to free glucose
- Solid conversion of Lignin & Pine increased by Lewis Acid catalysis
  - Gas phase products tend to syngas rather than alkanes
  - Minimal structural change of remaining Lignin (TGA, NMR, DRIFTS)
    - Some change in vibrational structure with La Triflate
  - Lignin/Gd Triflate demonstrates different decomposition mechanism

# LANL Proposed Future Work\* (FY09)

---

- Continue screening for novel hydrogen production catalysts
- Explore conversion chemistry of model monolignols
  - Develop heterogeneous catalyst for aqueous phase reactions
- Continue to explore lignin solubilization and pyrolysis
  - Investigate hydrophobic/hydrophilic effects on reaction chemistry of lignin
  - Improve homogeneous catalyst formulations

***\*Due to EERE Hydrogen Production and Delivery's budget being zeroed out, LANL is not currently funded for FY09***

# Obstacles to Lignocellulosic Conversion

---

- Conversion of solubilized hydrocarbons to vapor phase
- Conversion of model compounds simulating solubilization
- Unknown reactivity as a function of lignin pretreatment
- Lignin Solubilization
  - Interactions with catalysts limited
  - Hydrophobicity
  - Steric hinderance
- Conversion chemistry
  - Reaction mechanisms not understood
- Innovation in chemistry and catalysis
- Innovation in reactor design and reaction engineering

# Acknowledgements

---



**U.S. Department of Energy**  
**Energy Efficiency  
and Renewable Energy**

Bringing you a prosperous future where energy  
is clean, abundant, reliable, and affordable

**Hydrogen, Fuel Cells & Infrastructure Technologies  
Program: Hydrogen Production and Delivery  
Program Manager: Richard Farmer**